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CNDO/2 CALCULATIONS ON THE RELATIVE BASICITIES OF ALKYL BENZENES

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Abstract—CNDO/2 calculations were performed for toluene, ethyl benzene, iso-propyl benzene, t-butyl benzene, and neo-pentyl benzene, and the corresponding *ortho*, *meta*, and *para* protonated species. All rotational conformers against the benzene ring were examined and detailed energy differences and charge analyses are presented and discussed. The calculated energy differences suggest that for gas phase species the order of alkyl substituent rate enhancement for electrophilic aromatic reactions is t-Bu > i-Pr > Et > Me > H, thus the inductive order is found, rather than the hyperconjugative or Baker-Nathan order.

As a theoretical model for electrophilic aromatic substitution reactions, CNDO/2 molecular orbital calculations[1] were carried out on the species shown in Fig 1.

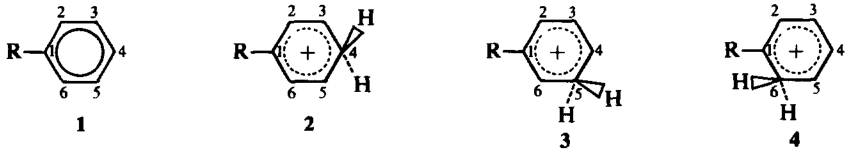


Fig 1.

The substituent R was systematically varied through the set of alkyl groups H, Me, Et, i-Pr, t-Bu, and neo-pentyl. The geometries of **1** were taken to be the standard geometries.[1] The geometries of **2–4** were taken to be identical with the corresponding geometry of **1** except at the site of protonation, where the angle between the geminal hydrogens (bond length 1·09 Å) was set at 101·5°, that angle required to make a set of two equivalent s-p hybrid orbitals orthogonal to another set with inclusive angle of 120°. The calculations were carried out on a CDC 3400 computer using a convergence criterion of 10^{-6} on each element of the density matrix. Calculations were performed for a variety of possible rotational conformers of the group R for all species except neo-pentyl. From these data the changes in energy and charge density associated with the three hypothetical gas phase reactions

$$\mathrm{H^+ + \mathbf{1} \rightarrow \mathbf{2}} \tag{1}$$

$$\mathrm{H^+ + \mathbf{1} \rightarrow \mathbf{3}} \tag{2}$$

$$\mathrm{H^+ + \mathbf{1} \rightarrow \mathbf{4},} \tag{3}$$

may be examined within the confines of the model employed.

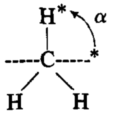
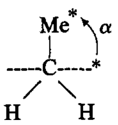
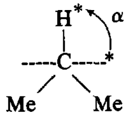
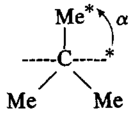
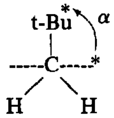
The model is, of course, highly approximate both with respect to the approximations inherent within CNDO/2 and with respect to the model geometries employed, and severe criticism can be raised on both points. However, it is certainly of interest to consider what changes occur within this model, since there is good reason to expect that the model will reflect the major features of substituent and conformational effects in many electrophilic aromatic substitution reactions. The CNDO/2 parameters[1] were originally determined to reliably reproduce electron densities and orbital energies obtained by more sophisticated calculations on a series of simple compounds. Recently Hehre and Pople[2] found that *ab-initio* minimal basis set calculations on a series of complex organic compounds including toluene give an electron density analysis paralleling that obtained by CNDO/2. Calculations based on the model used in this paper predict a difference of 11·2 kcal/mol between the proton affinities of toluene and benzene. This agrees favorably with the experimental value of 9·34 ± 3·37 kcal/mol obtained by Chong and Franklin.[3] Recent partial geometry optimization on the structure of protonated benzene by Helgstrand[4a] using CNDO/2 and INDO and by Hehre and Pople[4b] using *ab-initio* methods has yielded a σ protonated species not too dissimilar from that of this model. The major difference is in an elongation of the carbon–carbon bonds at the protonation site with the corresponding necessary decrease in the ring angle at that carbon. The *ab-initio* results gave an elongation of 0·07 Å with an angle decrease from 120° to 110·9°. The semi-empirical values were somewhat less than this. It is hard to see how these changes would alter the trends observed in this work.

Streitwieser *et al.*[5] applied virtually the identical model employed here in a relative study of protonation reactions on a wide variety of aromatic compounds and concluded that "The effect of methyl substituents is well accounted for by CNDO/2...".

The present study differs from that of Streitwieser *et al.*[5] in that this work is a detailed examination of energy and electron density changes in aromatic protonation reactions within a narrow class of compounds for which the model may be expected to be reasonably sound. Reference 5 was an application of CNDO/2 to a broad class of aromatic compounds to ascertain, in part, where the calculations were inapplicable.

Energy changes. Table 1 summarizes the calculated total energies for all species considered and for all rotational conformers examined. One point of some interest that can be extracted from these data is the calculated barrier to internal rotation of the alkyl group with the aromatic ring, within a frozen nuclear framework approximation. These values were 0·1, 3·1, 3·6, 1·0 and 23·7 kcal/mole for the respective alkyl groups Me, Et, i-Pr, t-Bu and neo-pentyl. The experimental values are 0·2[6] for Me and 1·3[7] kcal/mole for Et. The agreement between

Table 1. Calculated energies for the reactants and products of Fig 1

		Total energies (a.u.)			
Substituent[a]	$\alpha^{\circ b}$	Reactant	Product		
			Para	*Meta*	*Ortho*
-----H-----		−47·0979	−47·5564	−47·5564	−47·5564
	0	−55·7937	−56·2700	−56·2544	−56·2672
	30	−55·7937	−56·2700	−56·2541	−56·2668
	60	−55·7937	−56·2700	−56·2539	−56·2664
	0	−64·4807	−64·9580	−64·9431	−64·9557
	30	−64·4812	−64·9595	−64·9431	−64·9569
	60	−64·4845	−64·9646	−64·9458	−64·9603
	90	−64·4856	−64·9667	−64·9472	−64·9629
	120	−64·4845	−64·9646	−64·9466	−64·9616
	150	−64·4812	−64·9595	−64·9433	−64·9565
	180	−64·4807	−64·9580	−64·9427	−64·9549
	0	−73·1711	−73·6542	−73·6343	−73·6510
	30	−73·1692	−73·6516	−73·6321	−73·6482
	60	−73·1688	−73·6487	−73·6316	−73·6449
	90	−73·1653	−73·6454	−73·6285	−73·6430
	120	−73·1688	−73·6487	−73·6314	−73·6464
	150	−73·1692	−73·6516	−73·6320	−73·6486
	180	−73·1711	−73·6542	−73·6333	−73·6490
	0	−81·8519	−82·3356	−82·3165	−82·3333
	30	−81·8503	−82·3341	−82·3143	−82·3313
	60	−81·8519	−82·3356	−82·3155	−82·3310
	90	−90·5441	−91·0284	−91·0099	−91·0176
	180	−90·5064	−90·9870	−90·9789	−90·9828

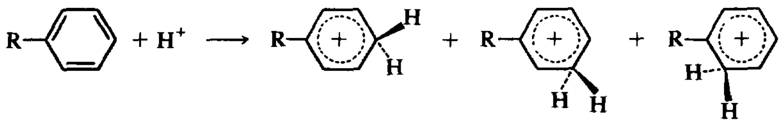
[a] An endview depiction of the substituent is shown in which the dotted line represents the plane of the benzene ring.

[b] α is the projected angle between the atom or group asterisked and the plane of the ring. In all *meta* and *ortho* cases, the carbon at which protonation occurs is eclipsed when $\alpha = 0$.

experimental and calculated values is adequate, suggesting that conformational energy effects in mono-alkyl benzenes may be satisfactorily described by this model. Previous work on rotational barriers within the CNDO/2 approximations[8] has found similar satisfactory agreement.

Of more interest are the relative stabilities of **1** and the protonated forms **2**, **3** and **4** as a function of substituent (Table 2). Fig 2 plots the difference in total energy between the protonated and unprotonated lowest energy conformers for the *ortho*, *meta*, and *para* forms versus the corresponding energy difference for the *para* form. It is apparent from the marked contrast between the nearly equal slopes of the lines for the *ortho* and *para* forms, and the very different slope of the nearly horizontal line for the *meta* forms, that the *ortho* and *para* protonations are considerably more influenced by substituent effects than is the *meta* protonation. This observation would be necessary for any credible theoretical model so that it is reassuring to find this decreased sensitivity to substituent changes in the *meta* case.

Table 2. Energy differences[a] between products and the reactants in the reaction



Substituent	Product					
	Para		*Meta*		*Ortho*	
	$\Delta_{EE}{}^{b}$	$(\Delta_{TE})^{b}$	$\Delta_{EE}{}^{b}$	$(\Delta_{TE})^{b}$	$\Delta_{EE}{}^{b}$	$(\Delta_{TE})^{b}$
H	−7·8094	(−0·4585)	−7·8094	(−0·4585)	−7·8094	(−0·4585)
Me	−8·4504	(−0·4763)	−8·5177	(−0·4607)	−8·8867	(−0·4735)
Et	−9·0244	(−0·4811)	−9·2349	(−0·4616)	−9·9697	(−0·4773)
i-Pr	−9·5816	(−0·4831)	−9·7937	(−0·4632)	−10·6994	(−0·4799)
t-Bu	−10·1509	(−0·4837)	−10·4274	(−0·4640)	−11·6374	(−0·4814)

[a] Energy differences are in atomic units

[b] Δ_{EE} is the electronic energy of the most stable conformer of the indicated product minus that for the most stable conformer of the reactant; Δ_{TE} is obtained in the same manner from the total energies.

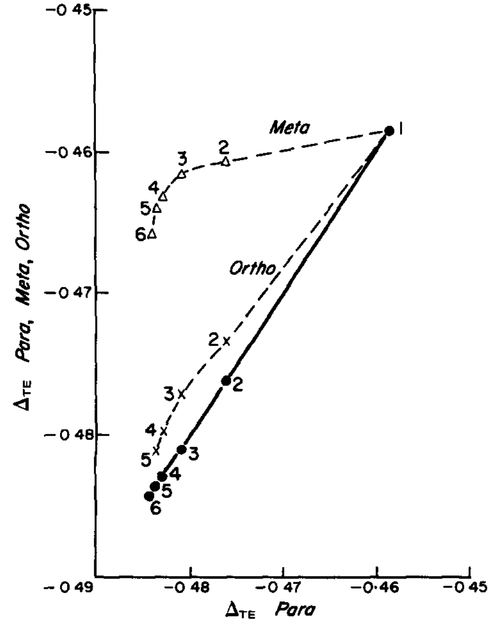


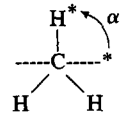
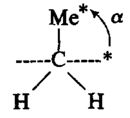
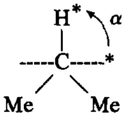
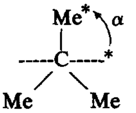
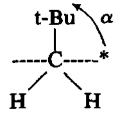
Fig 2. Δ_{TE} = energy of **2**, **3**, or **4** minus energy of **1**. Arabic integers correspond to: R = (1) H, (2) Me, (3) Et, (4) i-Pr, (5) t-Bu, and (6) neo-pentyl.

It is clear from Fig 2 that the present model establishes the inductive order t-bu > i-Pr > Et > Me for the relative stabilization of the protonated form over the unprotonated form for all three sites. This order is to be contrasted with the Baker-Nathan[9] or hyperconjugative order of rélative stabilization Me > Et > i-Pr > t-Bu. It has previously been established that, in solution phase protodetritiation reactions,[10] which of the above orderings of the relative rates of substitution was observed was a function of the solvent employed. Based upon substituent effects on gas phase electronic transitions, in contrast with those observed in various solvents, Shiner[11] and Schubert[12] have argued that the Baker-Nathan order is more of a solvent effect than it is intrinsic to substituent effects on the aromatic ring. Recently ion cyclotron resonance spectrometry has shown other reactions where the relative stabilizing effects of alkyl substituents in the gas phase differ from those in solution.[13] It has been found that the relative gas phase basicities of ammonia, aliphatic amines and pyridine differ from those found in solution.[14] In addition, substituent effects on the relative basicities of alkyl substituted pyridines are markedly attenuated in going from the gas phase to aqueous solution. Also the familiar order of acidities of alcohols is reversed in the gas phase. There the acidity order has been found to be t-BuOH > i-PrOH > EtOH > MeOH > HOH.[15] This is the order also predicted by CNDO/2.[16] The model calculations being reported here support the contention that the alkyl substituent effects on electrophilic aromatic substitution for gas phase species follow the inductive rather than the Baker-Nathan order.

Charge density changes. Table 3 presents the total net charge on each of the substituents for species **1** and the change in charge on the substituent upon passing to the species **2**, **3**, and **4**. Certainly one of the most outstanding features in the table is the tendency for the alkyl group to become more positive as one considers larger substituents. The neo-pentyl group, not being a continuous member of the family of successively substituted methyl groups, does not fit smoothly with the others, but is instead closely akin to the i-Pr group in its net electron density loss to the ring.

Before proceeding to a detailed examination of the charge density shifts, it is worthwhile to verify that there is indeed a correlation between some of the changes in charge density and the changes in energy. Fig 3 displays the change in charge on the substituent simultaneously with the change in energy as a function of the rotation of the ethyl group on benzene. It is very clear from the figure that as the change in charge on this substituent goes up (the substituent loses electron density to the ring), the total energy goes down. There is complete correlation between the change in energy on the

Table 3. Alkyl substituent charge of reactants (q) and changes in substituent charge (Δq)[a]

R	α^{0}[b]	q	Δq		
			Para	*Meta*	*Ortho*
-----H----		−0·0054	0·0680	0·0698	0·0653
	0	−0·0068	0·1394	0·0975	0·1349
	90	−0·0033	0·1359	0·0938	0·1304
	180	−0·0068	0·1394	0·0942	0·1332
	0	0·0024	0·1483	0·1047	0·1470
	30	0·0030	0·1492	0·1040	0·1444
	60	0·0045	0·1579	0·1040	0·1459
	90	0·0055	0·1523	0·1048	0·1479
	120	0·0045	0·1579	0·1047	0·1482
	150	0·0030	0·1492	0·1044	0·1457
	180	0·0024	0·1483	0·1048	0·1442
	0	0·0098	0·1641	0·1142	0·1629
	30	0·0095	0·1638	0·1139	0·1613
	60	0·0085	0·1623	0·1134	0·1579
	90	0·0073	0·1620	0·1137	0·1586
	120	0·0085	0·1623	0·1140	0·1629
	150	0·0095	0·1638	0·1136	0·1603
	180	0·0098	0·1641	0·1130	0·1584
	0	0·0127	0·1744	0·1223	0·1767
	90	0·0126	0·1743	0·1214	0·1726
	180	0·0127	0·1744	0·1209	0·1698
	90	0·0090	0·1674	0·1167	
	180	0·0081	0·1590	0·1273	0·1533

[a] Δq = charge on substituent of **2**, **3**, or **4** minus the charge on substituent of **1**.

[b] α is the same projected angle of Table 1.

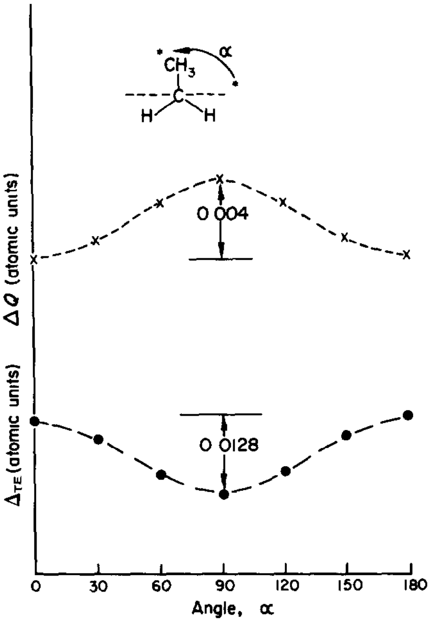


Fig 3. Δ_{TE} = energy of **2**, **3** or **4** minus energy of **1**. ΔQ = charge on substituent of **2**, **3**, or **4** minus charge on substituent of **1**.

substituent and the amount of electron density lost by this substituent to the ring.

It is worthwhile to take note of some of the quantitative relationships apparent in Table 3. Firstly the substituent loses more electron density to the ring when protonation occurs at the positions *ortho* or *para* to the substituent than it does when protonation occurs at the position *meta* to the substituent. This, of course, is also the ordering of the sensitivity of the total energy change to substituent as was displayed in Fig 2. All alkyl substituents release more electron density to the ring than does just a hydrogen. When R = t-Bu the density change for protonation at the *ortho* and *para* positions is almost three times the corresponding value when R = H. The *meta* protonations have similar relative changes but their absolute magnitudes are considerably smaller. It is clear from Table 3 that the greater the stabilization by the alkyl groups Me through t-Bu of the protonated over the unprotonated species, the greater the electron release of those alkyl groups to the ring. That is, electron release follows the order t-Bu > i-Pr > Et > Me > H.

It is natural to inquire in greater detail about where the electron density, which the alkyl substituent loses, originates within the substituent. Some especially interesting results appear from the data of Table 4 where the total net charge of the central C atom of the substituent for the species **1** and the changes in net charge upon going to species **2**, **3**, and **4** are presented. Most striking is that while the alkyl substituent loses electron density to the ring upon protonation, the central C atom of the substituent actually gains density becoming negative. For all three protonation sites this gain in electron density diminishes through the series Me, Et, i-Pr, t-Bu. However, in the *meta* protonation, the central alkyl C atom is negative only for the Me substituent and becomes slightly positive for the heavier substituents. Fig 4 presents a plot of this central alkyl atom change in net charge versus the corresponding change in the total energy for the lowest energy conformers for three protonations. The plot demonstrates the clear separation of the *meta* protonation from the *ortho* and *para*. There is a linear relationship between the central alkyl atom charge change and the corresponding change in total energy for the *para* protonation. For the *ortho* protonation the linearity extends only through the series Me, Et, i-Pr. The t-Bu substituent deviates from the linearity suggesting perhaps some steric factors entering into consideration. This latter thought is further borne out when it is noted that the lowest energy conformer for the i-Pr substituent is with the hydrogen eclipsing the site of protonation.

Another noteworthy feature which can be extracted from the data of Tables 3 and 4 is that the sum of the density lost by all the hydrogens when R = Me and by all the methyls when R = t-Bu shows essentially no conformational dependence, while the density lost by peripheral groups when R = Et and R = i-Pr is conformationally dependent. This point may be obtained from the tables by noting

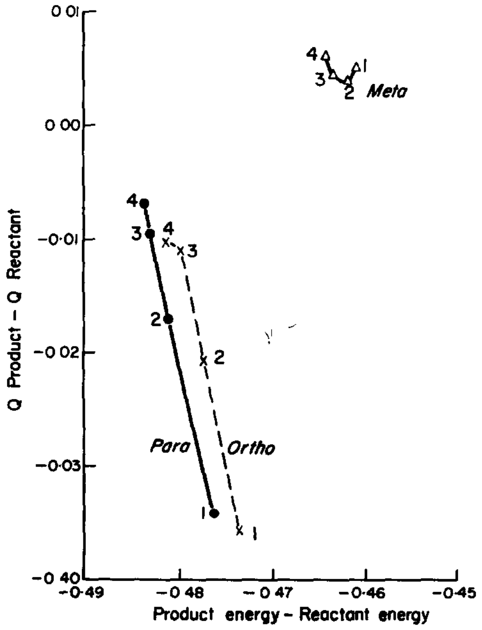
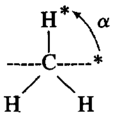
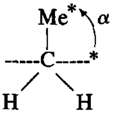
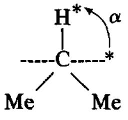
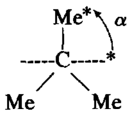


Fig 4. Q = charge on the substituent's central alkyl carbon. Arabic integers correspond to: R = (1) Me, (2) Et, (3) i-Pr, (4) t-Bu.

Table 4. Central alkyl carbon charge (q) of **1** and changes in central alkyl carbon charge (Δq)[a]

R	α°[b]	q	Δq		
			Para	*Meta*	*Ortho*
	0	−0·0206	−0·0343	−0·0052	−0·0360
	30	−0·0206	−0·0343	−0·0053	−0·0363
	60	−0·0206	−0·0343	−0·0054	−0·0365
	90	−0·0206	−0·0343	−0·0053	−0·0363
	120	−0·0206	−0·0343	−0 0052	−0·0360
	150	−0·0206	−0·0343	−0·0053	−0·0363
	180	−0·0206	−0·0343	−0·0054	−0·0365
	0	0·0084	−0·0263	−0·0001	−0·0311
	30	0·0102	−0·0242	0·0001	−0·0286
	60	0·0128	−0·0195	0·0005	−0·0241
	90	0·0138	−0·0171	0·0010	−0·0167
	120	0·0120	−0 0195	0·0012	−0·0212
	150	0·0102	−0·0242	0·0007	−0·0245
	180	0·0084	−0·0263	0·0008	−0·0264
	0	0·0364	−0·0095	0·0046	−0·0110
	30	0·0353	−0·0112	0·0045	−0·0131
	60	0·0331	−0·0148	0·0040	−0·0173
	90	0·0324	−0·0171	0·0037	−0·0202
	120	0·0331	−0·0148	0·0039	−0·0190
	150	0·0353	−0·0112	0·0041	−0·0166
	180	0·0364	−0·0095	0·0040	−0·0159
	0	0·0497	−0·0069	0·0062	−0·0104
	30	0·0498	−0·0070	0·0060	−0·0108
	60	0·0497	−0·0069	0·0060	−0·0113
	90	0·0498	−0·0070	0·0060	−0·0108
	120	0·0497	−0·0069	0·0062	−0·0104
	150	0·0498	−0·0070	0·0060	−0·0108
	180	0·0497	−0·0069	0·0060	−0·0113

[a] Δq = charge on central alkyl carbon of **2**, **3**, or **4** minus the charge on the central alkyl carbon of **1**.

[b] α is the same projected angle of Table 1.

that the difference between the total alkyl substituent charge and the central alkyl carbon charge is necessarily the charge on the periphery of the group. The variation by the Et and i-Pr groups suggests that, in addition to any possible inductive release by these groups, a conformationally dependent mode of release is operative. The invariance of the Me and t-Bu groups is consistent with a hyperconjugative release similar to that suggested by earlier authors.[17]

Having considered the loss of electron density by the substituent to the ring, the next consideration is where this density goes in the ring. Detailed charge analyses of the ring carbons in both the protonated and unprotonated species showed very little conformational dependence. It is possible to separate the changes in pi and sigma charge, and these separations were made and examined. The bulk of the positive charge in the protonated species is distributed about the ring in consonance with valence bond arguments, most of the charge residing at the positions *ortho* and *para* to the site of protonation. The sigma density shifts in opposition to that of the pi so as to reduce the net amount of positive charge at these sites, but the larger pi changes dominate. Table 5 summarizes these changes in the ring when R = Me. Similar trends were observed for R = Et, i-Pr and t-Bu.

To complete the analysis of net charges on the atoms, the ring hydrogen changes in net charge upon protonation were examined. Very little variation with substituent was observed. The change in charge at the hydrogens not at the site of protonation for the *para* reaction was a nearly constant 0·06. The two hydrogens at the site of the *para* protonation each bore a net charge change of 0·17 for benzene, which dropped to 0·15 regardless of substituent when species **2** was substituted.

SUMMARY

The detailed analyses of energy and charge density changes occurring within the model examined have

Table 5. Change in the charge of aromatic ring carbon atoms for reaction **1**→**2**, **1**→**3**, and **1**→**4** with R = Me: Total (pi)

	Atom number[a]					
Reaction	1	2	3	4	5	6
1→**2**	0·1660 (0 2908)	−0·0370 (−0·0436)	0·1298 (0·2217)	−0·0375 (0·0248)		
1→**3**	−0·0237 (−0·0275)	0·1657 (0·2928)	−0·0379 (−0·0465)	0·1439 (0·2443)	−0·0560 (0·0044)	0·1382 (0·2222)
1→**4**	0·1459 (0·2567)	−0·0460 (−0·0573)	0·1575 (0·2711)	−0·0305 (−0·0356)	0·1206 (0·2056)	−0·0379 (0·0314)

[a] The number scheme for the C atoms is the same as that of Fig 1.

brought out several major points. The degree of substituent stabilization of the developing positive charge in the Wheland intermediate follows the inductive order. There is a correlation between certain charge shifts upon protonation and the energy of stabilization. The charge released by the alkyl substituent in the ring also follows the inductive order. There is a nearly linear functional relation between the net charge change of the central alkyl carbon atom and the change in total energy for the *ortho* and *para* protonation, which is broken down only by apparent steric interactions for the *ortho* t-butyl case. This relationship is decidedly not valid for the *meta* protonation.

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